



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB93/02352 <b>(22) International Filing Date:</b> 16 November 1993 (16.11.93)  <b>(30) Priority Data:</b> 9225338.4                      3 December 1992 (03.12.92)                      GB  <b>(71) Applicant (for all designated States except US):</b> JEYES GROUP PLC [GB/GB]; Brunel Way, Thetford, Norfolk IP24 1HA (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> COOPER, Nigel, Frederick [GB/GB]; 25 Heywood Road, Diss, Norfolk IP22 3DJ (GB).  <b>(74) Agent:</b> LAMB, John, Baxter; Marks & Clerk, 57-60 Lincoln's Inn Fields, London WC2A 3LS (GB).		<b>(81) Designated States:</b> AU, BR, CA, GB, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LAVATORY CLEANSING BLOCKS  <b>(57) Abstract</b>  A solid lavatory cleansing block is formed of a composition comprising (A) from 5-8 % by weight of a surface active component comprising one or more anionic surface active agents; (B) from 10-75 % by weight of a halogen release agent component; and (C) from 1-25 % by weight of a liquid non-oxidisable material.		

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LAVATORY CLEANSING BLOCKS

This invention is concerned with improvements in and relating to lavatory cleansing blocks.

In particular, the present invention is concerned with solid lavatory cleansing blocks intended to be brought into contact with the flush water of a lavatory or urinal whereby a part of the block is dissolved in the flush water to release active ingredients thereto for cleaning the lavatory or urinal. The blocks are immersed in the water cistern of a lavatory or urinal, either as a free-standing block or may be placed or contained in a dispensing device, to be sited in a lavatory cistern. The invention is also concerned with lavatory cleansing blocks for intermittent contact with the flush water of a lavatory or urinal, e.g., a so-called "rim block" for placing in a container to be held under the rim of a lavatory, or a block to be placed in a container above a cistern for intermittent contact with, e.g. wash water, subsequently fed to the cistern.

One common class of component of lavatory cleansing blocks comprises one or more water-soluble surface

active agents. Another desirable component of such blocks would be a halogen release agent, that is a compound which on contact with water releases hypohalous acid and/or hypohalite ions to the water, since these are powerful sanitising and cleansing agents. In principle, there would appear to be no problem in combining these two classes of ingredient in a single block. However, halogen release agents are, by their nature, powerful chemically reactive species, serving as halogenating or oxidising agents. Thus, in practice, we have found that halogen release agents (i) tend to react with surface active materials and/or (ii) tend, when moistened, to evolve gas thereby losing their activity and, in many cases, destroying the physical integrity of the cleansing block. Further, halogen release agents may attack component parts of lavatories, urinals or their cisterns.

A particularly useful class of chlorine release agents comprises the N-chlorinated cyanuric acid derivatives such as sodium dichloroisocyanurate and trichlorisocyanuric acid. We have found in practice, however, that it is generally just not practically possible to reproducibly and reliably incorporate such chlorine release agents in a lavatory cleansing block in amounts sufficient to give useful cleansing and/or sanitising, e.g. amounts of 10% by weight or more.

We have now found, in accordance with the present invention, that the stability of blocks containing chlorinated cyanuric acid derivatives may be improved by incorporating therein a liquid non-oxidisable material. The term "liquid" as used herein is also intended to embrace relatively low melting materials, e.g. having a melting point of less than 60°C, which may become liquified (e.g. due to the action of heat and/or pressure) during the course of manufacture of the block.

According to the invention, therefore, there is provided a solid lavatory cleansing block formed of a composition comprising (A) from 5 to 80%, preferably from 10 to 70%, by weight of a surface active component comprising one or more anionic surface active agents; (B) from 10 to 75, preferably from 15 to 60% by weight of a halogen release agent component, preferably comprising one or more chlorinated cyanuric acid derivative chlorine release agents; and (C) from 1 to 25%, preferably from 4 to 15% by weight of liquid non-oxidisable material.

The block of the invention may also suitably contain a solubility control agent (as hereinafter defined). As discussed below, some of the non-oxidisable liquids may themselves serve as solubility control agents.

Preferably, the blocks of the invention contain no added filler (water-soluble or otherwise) other than that which may be introduced as contaminants or components of a surface active component. Accordingly, the blocks of the invention preferably contain not more than 20% by weight of water-soluble inorganic salts introduced by the anionic surface active agents and contain no added fillers or diluents.

Suitable anionic surface active agents for use in the blocks of the invention include alkali metal, typical sodium, paraffin sulphonates, olefin sulphonates, alkali metal alkyl sulphates and alkali metal alkaryl sulphonates, especially alkali metal benzene sulphonates. A typical example is sodium dodecyl benzene sulphonate which is a readily available material of commerce. The anionic surface active component of the block forms from 5 to 80% by weight of the composition, preferably from 10 to 70 % by weight thereof, most preferably from 25 to 65 % by weight thereof, and especially from 40 to 60% by weight thereof.

The halogen release component of the block is preferably an N-chlorinated cyanuric acid derivative, such as sodium dichloroisocyanurate or trichloroisocyanuric acid, especially the former. However other halogen release agents, such as calcium hypochlorite, may be employed.

The chlorine release component is present in the blocks of the invention in an amount of from 10 to 75% by weight, preferably from 15 to 70 % by weight, more preferably from 20 to 50 % by weight, and especially from 30 to 40% by weight.

The third component of the block is the non-oxidisable organic liquid. A wide variety of these may be employed, such as mineral oils, liquid hydrocarbons (e.g. liquid alkanes), chlorinated hydrocarbons, silicone oils, liquid ketones (e.g. 2-decanone), liquid tertiary alcohols (e.g. 2-methyl-hexan-2-ol), and liquid esters [(e.g. simple esters such as methyl decanoate, and more complex esters such as glycerol, propylene glycol, triethylene glycol esters of  $C_8$ - $C_{10}$  fatty acids and/or succinic acid. Examples of such complex esters are those sold under the trade names Miglyol 812, Miglyol 829, Miglyol 840, Plasthall 4141, Crodamol GTCC, Crodamol PC and Radia 7108.

The non-oxidisable organic liquid is of particular use for blocks intended to be manufactured, stored for use in non-temperate climates. The organic liquid also confers marked advantages for blocks intended for temperate climates. In this latter case, however, more oxidisable components may be present to assist in controlling block life.

A further possible component of the block is a solubility control agent, that is, a compound of lower solubility than the anionic surface active component and which assists in controlling the rate of dissolution of the block.

The solubility control agent may be virtually wholly insoluble in water or if, as discussed below a nonionic surface active agent, have a low HLB, e.g. 5 or less. Such agents should preferably be resistant to attack by the chlorine release component, both in the composition and in aqueous solutions produced by dissolution of the composition in use. It is a matter of simple experiment to determine whether any candidate is so resistant. Generally, the solubility control agent should be a saturated organic material or a highly chlorinated organic material. Examples of solubility agents which may be employed include polyethylene waxes; fatty alcohols; fatty acids; low ethoxylates (e.g. containing up to 4 ethylene oxide units per mole) of fatty alcohols and alkylphenols; paradichlorobenzene; and difficultly hydrolysable esters such as methyl salicylate and isobornyl acetate.

Certain of the solubility control agents noted above, the ethoxylated fatty alcohols and alkyl phenols, also possess surface active properties and thus may contribute to the overall cleansing effect of a



composition containing them. In this connection it may be noted that other nonionic surfactants may be present.

As noted above some of the non-oxidisable liquids may serve as solubility control agents. This is particularly true of the ketonic liquids and the esters, simple or complex. The more complex esters especially, tend to give good results when used as solubility control agents. The effectiveness of the non-oxidisable oils as solubility control agents may be modified, if desired, by using a relatively small amount, e.g. up to about 10% by weight, of another solubility control agent.

The blocks of the invention preferably do not contain more than 20% by weight of inert water-soluble salts, such as sodium sulphate, present as impurities introduced with the anionic surface active agent which is preferably not more than 75% and especially less than 10% by weight thereof. Commercially available anionic surface active agents often contain appreciable amounts of filler or diluent, such as sodium sulphate or sodium phosphate, and such commercially available materials may be used in formulating blocks in accordance with the invention to provided that in so doing too much salt is not introduced. However, in accordance with the invention, substantially no additional (e.g. less than 1% by weight) water-soluble or other filler should be

introduced, e.g., sodium sulphate, sodium carbonate, sodium tripolyphosphate, sodium bicarbonate, sodium metasilicate, sodium sesquicarbonate, sodium chloride, clays, calcite or the like.

It may be noted, however, that blocks intended for use in toilets having cisterns in which there is reduced turbulence, e.g. cisterns as found in toilets commonly used on the North American continent, can contain inert fillers in amounts of up to 30% by weight. Indeed, in this case the incorporation of a relatively dense mineral filler, such as calcium sulphate, may well increase the in-use life of the block. Further, the incorporation of certain metal salts, as disclosed for example in EP-A-0341836, can assist in improving stability of the blocks.

As will be appreciated, any other ingredient present in the composition of the invention should be resistant to attack by the chlorine release agent. Thus, for example, most dyestuffs commonly employed in lavatory cleansing blocks to impart a pleasant colouration to the flush water are not sufficiently resistant to the chlorine release agents with the results that (a) the dyestuffs are decolourised or discoloured to an unpleasant colour and (b) available halogen, which would otherwise serve as a sanitizing agent, is lost. However, there are indications that Acid Blue 7 may be

adequately resistant. Similarly, most perfumes which are commonly employed in lavatory cleansing blocks are also subject to attack by the chlorine release agents although some odiferous materials may be adequately resistant (and additionally serve as solubility control agents); examples of these being substituted quinolines, cedryl methyl ether and cineole.

Lavatory cleansing blocks commonly contain a germicide or preservative but this is not generally necessary in the case of the blocks of the invention since they already contain powerful germicides, namely the halogen release agents.

As noted above, it is not generally possible to incorporate dyestuffs or perfumes in the blocks of the invention. However, some insoluble pigments are resistant to the chlorine release agents and may be incorporated in the blocks of the invention to impart a colouration to the flush water. Examples of suitable pigments include copper phthalocyanine pigments which can be conveniently incorporated in the blocks of the invention in the forms of dispersions in suitable media.

The blocks of the invention are suitably formed by a compression process, especially an extrusion process comprising the steps of forming a mixture of the

components of the composition, extruding this mixture into rod or bar form and then cutting the extruded rod or bar into appropriately sized pieces or blocks. (In this connection it may be noted that a free standing lavatory cleansing block suitably has a weight of from 20 to 200 gms, preferably from 30 to 140 gms).

When producing blocks by an extrusion process it may be advantageous, from the point of view of extended stability of the block, to premix the chlorine release agent and liquid non-oxidisable material, whereby the particles of the chlorine release agent are coated with the non-oxidisable oil. Blocks in accordance with the invention may also be produced by tableting or by moulding a melt of the ingredients.

When an extrusion process is employed the mixture to be extruded should contain up to 25% by weight, of a liquid component or a solid component which is liquefied under extrusion conditions to act as a processing aid. In the case of the blocks of the invention this is conveniently provided by the use of the non-oxidisable liquid.

The invention also provides a method of cleansing a lavatory by intacting the flush water thereof with a block in accordance with the invention. The invention also provides doses of tablet treatment comprising

material having the formulation as described above and in particulate form and contained in a suitable container, e.g. a perforate or water-soluble container.

In order that the invention may be well understood the following examples are given by way of illustration only.

#### Examples 1 - 3

Free-standing lavatory cleansing blocks, each having a weight of about 55 gms, were made up, by extrusion, from formulations comprising 61.5% by weight of sodium dodecyl benzene sulphonate, 30.0% by weight of sodium diisochlorocyanurate and 8.5% by weight of a non-oxidisable oil, namely Miglyol 829 (Example 1), Plasthall 4141 (Example 2) and Crodamol PC (Example 3).

Each of the blocks had an in-cistern life, when tested at a rate of 17 flushes a day, of about 40 days.

#### Examples 4 - 10

Free-standing lavatory cleansing blocks were produced as described in Examples 1 - 3 from a mixture comprising 62% by weight of sodium dodecyl benzene sulphonate (Marlon A390), 30% by weight of sodium dichloroisocyanate and 8% by weight of non-oxidisable

oil as shown in Table I below. The blocks were stored at 37°/75% RH for two weeks and the percentage reduction in available chlorine level measured. The results are also shown in Table I.

TABLE I

Example	Non-oxidisable oil	% reduction in available chlorine
4	Miglyol 812	7.2%
5	Miglyol 829	10.1%
	Mineral oil (1%)	
6	Methyl dodecanate	0.8% (after 3 weeks)
7	Decane	0% (after 3 weeks)
8	2-Methyl-hexanol	11.3% (after 3 weeks)
9	2-Decanone	14.4% (after 3 weeks)

By way of comparison similar blocks not containing any non-oxidisable oil showed a 41.7% reduction in available chlorine after storage at 37°C for two weeks.

CLAIMS

1. A solid lavatory cleansing block formed of a composition comprising (A) from 5-8% by weight of a surface active component comprising one or more anionic surface active agents;  
(B) from 10-75% by weight of a halogen release agent component; and  
(C) from 1-25% by weight of a liquid non-oxidisable material.
2. A block as claimed in Claim 1 containing from 10-70% by weight of surface active component, of 15-60% by weight of halogen release component and from 4-15% by weight of liquid non-oxidisable material.
3. A composition as claimed in Claim 1 or Claim 2 in which the halogen release agent component comprises one or more chlorinated cyanuric acid derivative chlorine release agents.
4. A block as claimed in any one of the preceding claims in which the non-oxidisable oil is a mineral oil, liquid hydrocarbon, chlorinated hydrocarbon, silicone oil, liquid ketone, liquid tertiary alcohol or a liquid ester.
5. A block as claimed in any one of the preceding claims also containing a solubility control agent.

## INTERNATIONAL SEARCH REPORT

Int. Appl. No.  
PCT/GB 93/02352

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C11D17/00 A61L9/01 C11D3/395

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C11D A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 462 643 (UNILEVER) 27 December 1991 see claims; example 5 ---	1-5
X	WO,A,92 18605 (JEYES LTD.) 29 October 1992 see the whole document ---	1,3-5
P,X	EP,A,0 526 437 (KIWI BRANDS) 3 February 1993 see claims; examples 1,2,5 ---	1-5
A	GB,A,2 061 996 (JEYES LTD.) 20 May 1981 see examples; tables -----	1-5



Further documents are listed in the continuation of box C.



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NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Grittern, A



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0462643	27-12-91	AU-B- 628749 AU-A- 7838691 JP-A- 4252300	17-09-92 19-12-91 08-09-92
WO-A-9218605	29-10-92	AU-A- 1982192 CA-A- 2108975 EP-A- 0581826 GB-A- 2270084	17-11-92 23-10-92 09-02-94 02-03-94
EP-A-0526437	03-02-93	US-A- 5205955 AU-A- 1839892 JP-A- 5186799	27-04-93 07-01-93 27-07-93
GB-A-2061996	20-05-81	NONE	